

Organic Selenium Compounds

XVI.* Ultraviolet and Visible Spectroscopic Studies of Derivatives of Diselenocarbonic, Diselenocarbamic and Diselenothiocarbonic Acids

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The electronic absorption spectra of a number of organic derivatives of diselenocarbonic, diselenocarbamic, and diselenothiocarbonic acids have been studied in an attempt to assign the various visible and ultraviolet absorption bands to the possible electronic transitions. The nature of the shift of the bands on substituting the heteroatoms X=O, N, or S into the X-C(=Se)-Se- group, the shift of the bands with the change of solvent, and a comparison of the spectra with those of the corresponding thiocarbonyl compounds, have been used as criteria for assigning the bands to the $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, and $n \rightarrow \sigma^*$ transitions. A band due to the Se-Se chromophoric group is recognized, and classification of the bands and their intensities is included. The study supports the view that the nature of the arrangement of electrons in the selenium atom is similar to that of sulfur and the electrons in the former are more weakly bound.

The organoselenocarbonyl ($>C=Se$) compounds have been the subject of comparatively little study, although they have been known for more than 50 years. In a recent review article, King¹ has pointed out that this situation is because "The organic selenium compounds are much less stable than their sulfur analogues and chemists have much less experience in handling them".

It is well known that earlier attempts^{2,3} to prepare selenoaldehydes and selenoketones have been unsuccessful because of their tendency to form cyclic polymers, thereby destroying the C=Se linkage. It was thought, therefore, that large organic molecules,⁴ containing the $>C=Se$ group, might be used in a study of the electronic structure of this chromophoric group. Recently, Jensen *et al.*,⁵⁻⁹ Pedersen,¹⁰ Rosenbaum *et al.*,¹¹ Renson *et al.*,^{12,13} Barnard

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and Woodbridge,¹⁴ and the author have described the synthesis of a large number of selenocarbonyl compounds.

The most striking physical property of these compounds is their colour which generally varies between yellow and orange. No information is available on the absorption maxima in the visible regions for the aliphatic selenocarbonyl compounds; recently, however, Franosini¹⁵ reported that the visible absorption band for an aromatic compound, 2,6-dimethyl-4-seleno- γ -pyrone occurred around 650 nm. Mautner *et al.*,¹⁶ Renson and coworkers,^{12,13} and Barnard and Woodbridge,¹⁴ have reported the absorption maxima of some of the strong absorption bands in the near ultraviolet region for some compounds in which the $>C=Se$ group is linked to nitrogen atom(s).

In earlier publications,^{17,18} the electronic spectra of the derivatives of di- and trithiocarbonic acid ($-X-C(=S)-S-$; $X=S, O, \text{ or } N$) were studied. It is the purpose of the present investigations to extend these studies to the corresponding derivatives of diselenocarbonic ($-O-C(=Se)-Se-$), diselenocarbamic ($>N-C(=Se)-Se-$), and diselenothiocabonic ($-S-C(=Se)-Se$) acids. It is believed that the data would be useful for purposes of comparison, and also in enlarging our knowledge on the elements of the VI group of the periodic table. This study attempts to assign, on the basis of the solvent effect, the various absorption bands observed to the $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ electronic transitions, to correlate these data with the information available on the corresponding thiocarbonyl derivatives, and also to rationalize the shifts of the bands observed when the $C=Se$ group is conjugated with monoatomic substituents ($O, N, \text{ or } S$) bearing lone pairs of electrons.

EXPERIMENTAL

Compounds

Derivatives of diselenocarbonic acid. Potassium ethyldiselenoxanthate (potassium *O*-ethyl diselenocarbonate) was prepared by reacting potassium ethanolate and carbon diselenide.^{19,9} *Se*-Carboxymethyl esters of *O*-alkyl diselenocarbonic acid ($RO-C(=Se)-Se-CH_2COOH$) in which $R=C_2H_5, n-C_3H_7, \text{ or } i-C_3H_7$ were prepared in this laboratory in connection with other studies.⁹ Bis(ethoxyselenocarbonyl) diselenide ($(C_2H_5O-C(=Se)-Se)_2$; m.p. 62°C) was prepared by the oxidation of potassium ethyldiselenoxanthate in water with ammonium persulfate. This compound has been previously prepared by the oxidation of potassium ethyldiselenoxanthate with iodine.¹⁴

Derivatives of diselenocarbamic acid. Sodium *N,N*-diethyldiselenocarbamate, diethylammonium *N,N*-diethyldiselenocarbamate, dipropylammonium *N,N*-dipropyldiselenocarbamate, and piperidinium 1-piperidinecarbodiselenoate were prepared according to Rosenbaum *et al.*¹¹ Morpholinium 4-morpholinecarbodiselenoate and pyrrolidinium 1-pyrrolidinecarbodiselenoate, carboxymethyl *N,N*-diethyl-, and *N,N*-dipropyldiselenocarbamates, carboxymethyl piperidine-, morpholine-, and pyrrolidinecarbodiselenoates were prepared and purified as described earlier.⁴

Derivatives of diselenothiocabonic acid. Carboxymethyl *S*-isopropyl and carboxymethyl *S*-isobutyl diselenothiocabonates were prepared according to Jensen and Anthoni.²⁰

Solvents

Ethanol was purified by refluxing with sodium hydroxide and was used only after subsequent distillation. Methylene chloride and heptane were supplied by Riedel-De Haën AG., Seelze-Hannover, and they were distilled once before use. Methyl cyanide

Table 1. Peak wavelengths and molar extinction coefficients for some derivatives of diselenocarbonic acid.

Compound	Water		Ethanol		Dichloro- methane		Heptane		Methyl cyanide	
	λ_{\max} nm	$\log \epsilon$	λ_{\max} nm	$\log \epsilon$	λ_{\max} nm	$\log \epsilon$	λ_{\max} nm	$\log \epsilon$	λ_{\max} nm	$\log \epsilon$
EtOCSe ₂ K	452	2.12	458	2.26	—	—	—	—	—	—
	350	4.11	354	4.12	—	—	—	—	—	—
	253	3.91	253	3.99	—	—	—	—	—	—
EtOCSe ₂ CH ₂ COOH			425	2.38	—	—	433	2.09	425	2.10
			324	4.15	—	—	319	4.33	323	4.20
			244	4.20	—	—	243	4.34	243	4.30
PrOCSe ₂ CH ₂ COOH			424	2.12	424	2.06	434	2.00	424	2.12
			325	3.83	324	3.88	321	4.00	323	4.13
			246	3.89	245	3.91	244	4.01	243	4.11
Pr ⁱ OCSe ₂ CH ₂ COOH			424	2.16	426	2.10	434	1.97	424	2.21
			325	3.81	324	3.82	321	3.93	323.5	3.99
			245	3.85	245	3.86	243	3.94	243	3.98
EtOC(Se)Se—SeC(Se)OEt			432sh	2.40			440	2.39	434sh	2.40
			347sh	4.05			340sh	—	345sh	4.20
			295	4.42			297	4.43	296	4.50
			239	4.20			242	4.18	238	4.31

sh = shoulder

was of a spectrograde quality supplied by Carlo Erba Company, Italy. Diethyl ether was freed from peroxides by shaking with iron(II) sulfate and then washed with water. It was kept over anhydrous calcium chloride and later refluxed with sodium to remove traces of water, and distilled. Doubly distilled water was used.

Spectra

The ultraviolet and visible absorption spectra of solutions were recorded on a Perkin Elmer Model 137 spectrophotometer, using 1 cm fused quartz matched cells. The temperature of the cells was maintained at 20°C. A concentration range from 5×10^{-5} M to 1×10^{-2} M was used. The spectra of some of the carboxymethyl derivatives (*O*-ethyl diselenocarbonate, 1-piperidinecarbodiselenoate and *S*-isopropyl diselenothiocarbonate) were studied in 96% analytical grade sulfuric acid. During such studies the compound was dissolved in the acid at 0°C and the spectra measured within 10 min. However, the acid could not be used as a solvent for the remaining compounds since they decomposed in the acid medium, resulting in the precipitation of red selenium.

RESULTS

The data on the absorption maxima (nm) and the molar extinction coefficients ($\log \epsilon$) of the various compounds investigated are included in Tables

Table 2. Peak wavelengths and molar extinction coefficients for some derivatives of diselenocarbamic acid.

Compound	Water		Ethanol		Dichloro- methane		Diethyl ether		Methyl cyanide	
	λ_{\max} nm	$\log \epsilon$	λ_{\max} nm	$\log \epsilon$	λ_{\max} nm	$\log \epsilon$	λ_{\max} nm	$\log \epsilon$	λ_{\max} nm	$\log \epsilon$
Et ₂ NCSe ₂ Na	403	2.20	415	2.18						
	318	4.06	328	4.05						
	274	4.20	277	4.18						
[Et ₂ NCSe ₂][H ₂ NEt ₂]	403	2.19	415	2.20						
	318	4.35	327	3.77						
	275	4.52	280	3.93						
[Pr ₂ NCSe ₂][H ₂ NPr ₂]	404	2.10	416	2.15						
	318	4.10	326	3.78						
	274	4.51	281	4.20						
[C ₅ H ₁₀ NCSe ₂][H ₂ NC ₅ H ₁₀]	404	2.25	416	2.30						
	317	3.97	325	3.90						
	277.5	4.17	281	4.20						
[(CH ₂) ₄ NCSe ₂][H ₂ N(CH ₂) ₄]	384	2.32	390	2.28						
	314	3.93	318	3.95						
	271	4.07	278	4.10						
[O(CH ₂) ₄ NCSe ₂][H ₂ N(CH ₂) ₄ O]	404	2.10	416	2.14						
	318	3.98	325	4.00						
	276	4.10	280	4.15						
Et ₂ NCSe ₂ CH ₂ COOH	—	—	388	2.21	375	2.20	400	2.20	382	2.28
	—	—	314	4.03	313	4.08	317	3.96	312	4.08
	—	—	267	4.08	265	4.13	265	4.04	265	4.12
	—	—	256	4.10	255	4.16	255	4.06	254	4.15
Pr ₂ NCSe ₂ CH ₂ COOH	—	—	390	2.20	374	2.10	401	2.15	—	—
	—	—	315	4.10	314	4.15	316	4.10	—	—
	—	—	265	4.00	265	4.10	265	4.10	—	—
	—	—	255	4.10	255	4.00	253	4.12	—	—
C ₅ H ₁₀ NCSe ₂ CH ₂ COOH	—	—	388	2.19	372	2.20	400	2.19	380	2.30
	—	—	314	3.96	313	4.03	317	4.14	313	4.03
	—	—	266sh	3.97	265	4.08	265	4.19	265	4.04
	—	—	255	3.99	255	4.10	253	4.23	253	4.06
O(CH ₂) ₄ NCSe ₂ CH ₂ COOH	—	—	395	2.20	372	2.21	402	2.14	392	2.01
	—	—	314	4.09	315	4.11	317	4.09	315	4.08
	—	—	273	4.08	272	4.09	270	4.20	275	4.10
	—	—	256	4.08	—	—	262	4.18	254	4.09
(CH ₂) ₄ NCSe ₂ CH ₂ COOH	—	—	380	2.22	—	—	—	—	—	—
	—	—	310	3.90	—	—	—	—	—	—
	—	—	262sh	3.98	—	—	—	—	—	—
	—	—	255	4.00	—	—	—	—	—	—

sh = shoulder

Table 3. Peak wavelengths and molar extinction coefficients of some carboxymethyl esters of diselenothiocarbonic acid.

Compound	Ethanol		Methylene chloride		Methyl cyanide		Heptane	
	λ_{\max} nm	$\log \epsilon$	λ_{\max} nm	$\log \epsilon$	λ_{\max} nm	$\log \epsilon$	λ_{\max} nm	$\log \epsilon$
Pr ⁱ SCSe ₂ CH ₂ COOH	534	1.92	534	2.00	—	—	541	1.92
	365	3.87	361	3.89	—	—	357	3.87
	323	3.90	324	3.92	—	—	325	4.00
Bu ⁱ SCSe ₂ CH ₂ COOH	534	1.93	534	2.06	532	1.80	540	1.98
	366	3.89	362	3.84	365	3.71	358	3.98
	323	3.92	324	4.06	324	3.80	325	4.08

1 to 3. Representative absorption spectral curves of a covalent compound of diselenothiocarbonic acid, an ionic and two covalent compounds of diselenocarbonic, and an ionic and a covalent compound of diselenocarbamic acid are given in Figs. 1 to 6.

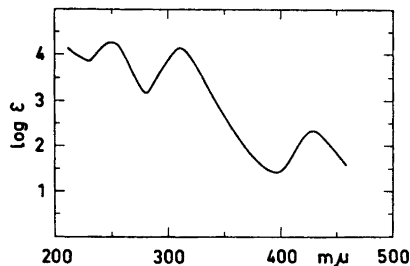
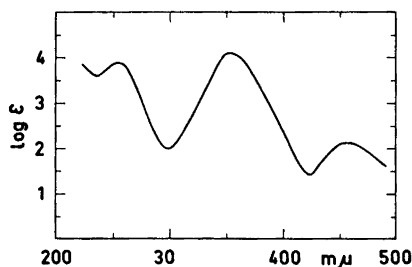


Fig. 1. Spectrum of C₂H₅OCSe₂K in ethanol. Fig. 2. Spectrum of C₂H₅OCSe₂COOH in ethanol.

DISCUSSION

An examination of Tables 1 to 3 and Figs. 1 to 6 shows that all the derivatives of the diselenocarbonic, diselenocarbamic, and diselenothiocarbonic acids exhibit a low intensity band in the visible region of the spectrum. In addition, two strong absorption bands are found in the spectra of the derivatives of diselenocarbonic and diselenothiocarbonic acids while three strong absorption bands are found in those of the diselenocarbamic acid. For convenience, and also for an easy classification of the various bands, the data included in the Tables 1 to 3 are summarized in the Table 4. Data on the absorption maxima of the corresponding thiocarbonyl compounds are also included in the table for purposes of comparison.

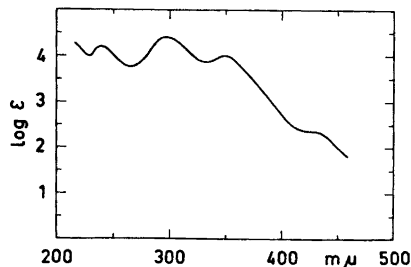


Fig. 3. Spectrum of $C_2H_5OC(Se)Se-Se-C(Se)OC_2H_5$ in ethanol.

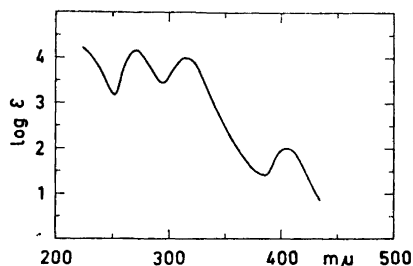


Fig. 4. Spectrum of $(C_2H_5)_2NCSe_2Na$ in ethanol.

Table 4. Data on the absorption bands of the selenocarbonyl and thiocarbonyl covalent compounds with the structure $-X-C(=Y)-Y-$.

No.	Compound	Atoms		Absorption maxima in nm			
		X	Y	I	II	III	IV
1(a)	Diselenothiocarbonate	S	Se	540		358	324
	Trithiocarbonate	S	S	429		303	238
2(a)	Diselenocarbonate	O	Se	434		320	243
	Dithiocarbonate	O	S	357		278	221
3(a)	Diselenocarbamate	N	Se	400	317	266	255
	Dithiocarbamate	N	S	343	277	246	224

In Table 4, the low intensity band is designated as band I while the remaining strong absorption bands are designated II, III, and IV.

Band I. The spectra of all the compounds exhibit this low intensity band ($\log \epsilon \approx 2.2$) at longer wavelengths. This band is the most novel and, at the same time, important from the point of view of assignment as the position of

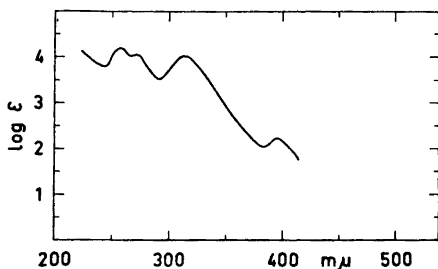


Fig. 5. Spectrum of $(C_2H_5)_2NCSe_2CH_2COOH$ in ethanol.

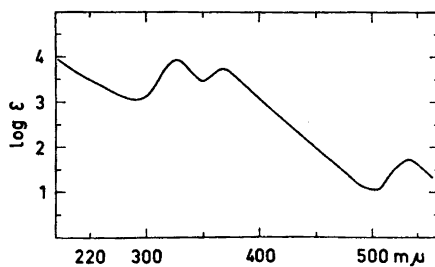
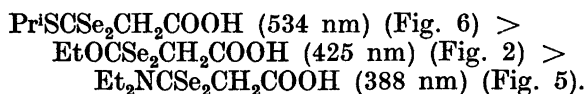


Fig. 6. Spectrum of $i-C_3H_7SCSe_2CH_2COOH$ in ethanol.

it is markedly dependent on the atoms linked to the $>C=Se$ group. The band is very sensitive to the solvent used and it shifts to shorter wavelengths on passing from non-polar to polar solvents. The band disappeared when the spectra of the *Se*-carboxymethyl derivatives (*O*-ethyl diselenocarbonate, 1-piperidinecarbodiselenoate, and *S*-isopropyl diselenothiocarbonate) were studied in concentrated sulfuric acid. The band also moves towards shorter wavelengths on substitution of the heteroatom (X) into the $-X-C(=S)-Se-$ group (where X = S, O, or N); the shift being a maximum when X = N. The above findings suggest that the low intensity band arises from the promotion of a non-bonding electron ($4p_y$), localized on the selenium atom of the $>C=Se$ group, to an antibonding π -molecular orbital. The transition is labelled as $n \rightarrow \pi^*$ transition.²²⁻²⁵ The direct proportionality between the blue shift of the band and the polarity of the solvent indicates that the transition energy involved increases with the increase in polarity of the solvent, due to solvation and/or hydrogen bonding between the non-bonding electrons of the $>C=Se$ group of the solute and the solvent molecules.

2,6-Dimethyl 4-seleno- γ -pyrone¹⁵ has been found to exhibit a long wavelength band at 650 nm. This band may be assigned to the $n \rightarrow \pi^*$ transition, and the shift towards longer wavelengths can be explained in terms of conjugation. Similar bathochromic shifts have been observed in carbonyl²⁶ and thiocarbonyl²⁷ compounds.

The electronic configuration of selenium is known to be similar to that of sulfur and oxygen. One should, therefore, expect the selenocarbonyl group to absorb at wavelengths longer than that of the thiocarbonyl and carbonyl groups because the $4p_y$ electron of the selenium is more weakly bound than that of the $3p_y$ and $2p_y$ electron of the sulfur and oxygen, respectively. The ionization potential of the selenium atom is 9.5 V while that of sulfur and oxygen atoms are 10.3 and 13.6 V, respectively.^{28,29} Because of this, the energy required for the excitation of the non-bonded electron of selenium is less than the energy required for the excitation of the non-bonded electron of sulfur (Table 4) and oxygen.²³ Potassium *O*-ethyl diselenocarbonate (Fig. 1) shows an absorption maximum at 458 nm in ethanol, while potassium *O*-ethyl dithiocarbonate³⁰ absorbs, in the same solvent, at 383 nm. Similarly, sodium *N,N*-diethyldiselenocarbamate (Fig. 4) and *Se*-carboxymethyl *S*-isopropyl diselenothiocarbonate in ethanol (Fig. 6) absorb at 415 and 534 nm, respectively (Tables 2 and 3), and their sulfur analogues^{30,31} in the same medium, at 359 and 430 nm, respectively. Further, the parallel spectral behaviour of the selenocarbonyl and the thiocarbonyl groups can be seen from the data (Table 4) on the intramolecular blue shift of the $n \rightarrow \pi^*$ transition bands produced by the electron donating substituents. The $n \rightarrow \pi^*$ band of the $>C=Se$ group in the derivatives containing the $-X-C(=Se)-Se-$ (X = S, O, or N) group shifts progressively to shorter wavelengths in the following sequence:



Consequently, the substituent heteroatom (S, O, or N), possessing a lone pair of electrons, acts as an electron donor (by resonance) to the $>C=Se$ group

resulting in a blue shift of the $n \rightarrow \pi^*$ band in these compounds. A similar behaviour of the mesomeric electron releasing order $S < O < N$ has been observed in the corresponding thiocarbonyl^{18,21,31,32} and carbonyl³³ compounds. In the derivatives of the diselenocarbamic acid, the substitution of the dialkyl-amino groups with piperidino or morpholino groups did not alter greatly the position of the various bands. However, introduction of the 1-pyrrolidyl group shifts all the bands towards shorter wavelengths. This hypsochromic shift may be due to a greater electron-donating tendency of the 1-pyrrolidyl group in the excited state. A similar effect, caused by a 1-pyrrolidyl group, has also been found in compounds containing the thiocarbonyl group.³¹

Strong absorption bands in the near ultraviolet region

The bands II, III, and IV (Tables 1, 2, 3, and 4) have nearly the same intensity.

Band II. This band is present only in the derivatives of the diselenocarbamic acid (and also in compounds where the $>C=Se$ group is directly linked to nitrogen atom(s) such as selenoamides, *O*-alkyl selenocarbamates, selenosemicarbazides and selenoureas³⁴). The band was found to disappear from the spectrum of carboxymethyl piperidinecarbodiselenoate when it was measured in concentrated sulfuric acid. The band shifts towards lower wavelengths on changing the solvent from diethyl ether to ethanol. It is interesting to note that a similar band is found in the derivatives of dithiocarbamic acid^{18,21,31} and also in other nitrogen containing thiocarbonyl compounds.³⁵ Because of the direct relationship of the blue shift of this band to the polarity of the solvent it is tempting to suggest that the origin of the band may be an $n \rightarrow \sigma^*$ transition.

The band situated at 287 nm in the selenosemicarbazone of butyraldehyde is found at 327 nm in the selenosemicarbazone of benzaldehyde.¹³ The bathochromic shift on conjugation with a benzene ring supports the suggestion that the band may arise from a $\pi \rightarrow \pi^*$ transition. Recently, Sandström³⁶ used the bathochromic shift of the band on conjugation to assign the 279 nm band of methyl dithiocarbamate to a $\pi \rightarrow \pi^*$ transition. It is known that the $\pi \rightarrow \pi^*$ band can also exhibit a blue shift on increasing the polarity of the solvent.²⁴ However, band II may be ascribed as characteristic of the $N-C=Se$ group since a similar band with the same behaviour is also found in the other nitrogen containing selenocarbonyl compounds — such as selenoureas, selenosemicarbazides, and *O*-alkyl selenocarbamates.³⁴

Band III. This band is observed in all the compounds studied in this paper. The band shows generally small red shifts when the solvent is changed from a non-polar to a polar solvent. On the basis of both solvent effect studies and data on corresponding sulfur compounds,^{18,21} the band may be assigned to a $\pi \rightarrow \pi^*$ transition in which an electron is excited from the highest occupied π -orbital to the lowest and empty antibonding π -level. In the case of diselenocarbamate compounds, band III (around 266 nm) may be considered as due to a second $\pi \rightarrow \pi^*$ transition. It is interesting to note that band III immediately precedes band I ($n \rightarrow \pi^*$) in all the compounds studied except in the derivatives

of the diselenocarbamic acid. In carboxymethyl esters of diselenocarbamic acid band III occurs only as a shoulder. As with the $n \rightarrow \pi^*$ band, the $\pi \rightarrow \pi^*$ band also shifts towards shorter wavelengths on increasing the electron releasing tendency of the substituent atoms linked to the $C=Se$ group.

The bands occurring at 318 and 285 nm in zinc diethyl diselenocarbamate^{14,39} correspond, respectively, to the bands around 317 nm (band II) and 276 nm (band III) present in the ionic diselenocarbamate compounds (Table 2). The fact that these bands are not shifted in the zinc complex indicates that they arise from internal transitions within the ligands. In the covalent organic compounds of diselenocarbamic acid band III is not well resolved because of the close proximity of an intense band (band IV).

Band IV. The derivatives of diselenothiocarbamic acid exhibit this band at 324 nm, whilst in the derivatives of diselenocarbamic and the diselenocarbamic acids it occurs around 243 and 255 nm, respectively. The intense band occurring around 253 nm in the alkali metal diselenocarbonates shifts to 295 nm in bis(ethoxyselenocarbonyl)diselenide (Fig. 3). The 295 nm band shows a blue shift on changing the solvent from heptane to ethanol. It is known^{23,37} that compounds of the type $R-A-A-R'$ with overlapping lone pair of electrons absorb at longer wavelengths than analogous compounds of the type $R-A-R'$. Thus a diselenide absorbs at longer wavelengths than a corresponding monoselenide.

The band can therefore be ascribed to an $n \rightarrow \sigma^*$ transition within the $Se-Se$ chromophoric group. In this process an electron transfer may take place either from the non-bonding lone pair, localized in the $Se-Se$ group, to an antibonding σ -orbital within the group, or from the antibonding π -orbital (formed by the combination of the lone pair of electrons) to the antibonding σ -orbital.^{37,38}

In addition to the bands discussed above other bands were observed in some of the compounds; these are not included in the Tables 1–3. For example, the band corresponding to the 240 nm band of bis(ethoxyselenocarbonyl)diselenide occurs around 213 nm in both the alkali metal *O*-ethyl diselenocarbonates and in *O*-alkyl *Se*-carboxymethyl esters of diselenocarbamic acid. In the case of these carboxymethyl esters the 213 nm band was absent in heptane solution. In the ionic diselenocarbamate compounds a band corresponding to band IV appears to merge with band III to form a composite band. No attempt was made to study these bands because of the practical difficulties, such as choosing the solvents, and the unreliability of the data in such wavelength regions.

Work is in progress on the LCAO–MO calculations of the $>C=Se$ group linked to different heteroatoms.

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REFERENCES

1. King, H. K. *Science Progress* **50** (1962) 629.
2. Vanino, L. and Schinner, A. *J. prakt. Chem.* **91** (1915) 116.
3. Bradt, W. E. *J. Chem. Educ.* **12** (1935) 363.

4. Shankaranarayana, M. L. *Acta Chem. Scand.* **24** (1970) 351.
5. Jensen, K. A., Felbert, G. and Kägi, B. *Acta Chem. Scand.* **20** (1966) 281.
6. Jensen, K. A., Felbert, G., Pedersen, C. Th. and Svanholm, U. *Acta Chem. Scand.* **20** (1966) 278.
7. Jensen, K. A. *Acta Chem. Scand.* **17** (1963) 551.
8. Jensen, K. A. and Nielsen, P. H. *Acta Chem. Scand.* **20** (1966) 597.
9. Jensen, K. A., Frederiksen, P. A. A. and Henriksen, L. *Acta Chem. Scand.* **24** (1970) 2061.
10. Pedersen, C. Th. *Acta Chem. Scand.* **17** (1963) 1459.
11. Rosenbaum, V. A., Kirchberg, H. and Leibnitz, E. *J. prakt. Chem.* **19** (1963) 1.
12. Collard-Charon, C. and Renson, M. *Bull. Soc. Chim. Belges* **72** (1963) 149.
13. Huls, R. and Renson, M. *Bull. Soc. Chim. Belges* **66** (1957) 55.
14. Barnard, D. and Woodbridge, D. T. *J. Chem. Soc.* **1961** 2922.
15. Franosini, P. *Gazz. Chim. Ital.* **88** (1958) 1109.
16. Mautner, H. G. and Kumler, W. D. *J. Am. Chem. Soc.* **78** (1956) 97.
17. Shankaranarayana, M. L. and Patel, C. C. *Can. J. Chem.* **39** (1961) 2590.
18. Shankaranarayana, M. L. and Patel, C. C. *Acta Chem. Scand.* **19** (1965) 1113.
19. Grimm, H. G. and Metzger, H. *Ber.* **69** (1936) 1356.
20. Jensen, K. A. and Anthoni, U. *Acta Chem. Scand.* **24** (1970) 2055.
21. Janssen, M. J. *Rec. Trav. Chim.* **79** (1960) 464.
22. Rao, C. N. R. *Ultraviolet and visible spectroscopy*, Butterworths, London 1961.
23. Mason, S. F. *Quart. Rev. (London)* **17** (1963) 20.
24. Sidman, J. W. *Chem. Rev.* **58** (1959) 689.
25. Kasha, M. *Discussions Faraday Soc.* **9** (1950) 14.
26. McClure, D. S. and Hanst, P. L. *J. Chem. Phys.* **23** (1955) 1772.
27. Brocklehurst, P. and Burawoy, A. *Tetrahedron* **10** (1960) 118.
28. Price, W. C. *J. Chem. Phys.* **16** (1948) 551.
29. Murrel, J. N. *The theory of the electronic spectra of organic molecules*, Wiley, New York 1963.
30. Janssen, M. J., Balasubramanian, A. and Rao, C. N. R. *J. Sci. Ind. Res. (India)* **B 20** (1961) 349.
31. Janssen, M. J. *The Electronic Structure of Organic Thion Compounds*, Doctoral Thesis, Utrecht 1959.
32. Rao, C. N. R., Balasubramanian, A. and Ramachandran, J. *J. Sci. Ind. Res. (India)* **B 20** (1961) 382.
33. Nagakura, S. *Bull. Chem. Soc. Japan* **25** (1952) 164.
34. Shankaranarayana, M. L. *Unpublished results*.
35. Janssen, M. J. *Rec. Trav. Chim.* **79** (1960) 454.
36. Sandström, J. *Acta Chem. Scand.* **16** (1962) 1616.
37. Bergson, G., Claeson, G. and Schotte, L. *Acta Chem. Scand.* **16** (1962) 1159.
38. Bergson, G. *Some New Aspects of Organic Disulphides, Diselenides and Related Compounds*, Abstracts of Uppsala Dissertations in *Science* **13** (1962).
39. Jensen, K. A., Krishnan, V. and Jørgensen, C. K. *Acta Chem. Scand.* **24** (1970) 743.

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